SCIENCE FOR CERAMIC PRODUCTION

UDC 666.291.5:666.3-431

METHODS OF DYEING CERAMIC BRICK

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Translated from *Steklo i Keramika*, No. 8, pp. 15 – 18, August, 2007.

The results of a study of the possibility of bulk dyeing of ceramic brick by incorporating manganese and iron ore and metallic slags and sludges from electroplating plants in the pastes are reported. It was found that low-melting clays should first be bleached with chalk or fireclay or kaolin impregnated with solutions of transition metal salts in order to attain a broad color scale for the articles. Using natural raw materials and soluble salts of 3*d* elements significantly expands the raw-materials base, reduces the cost of the ceramic articles by replacing expensive materials, and combines synthesis of pigments and firing of the articles.

One of the most important problems in production of ceramic brick concerns manufacturing articles with a uniformly colored, monochromatic face.

The clays used in production of the brick contain soluble salts, carbonates in particular, and their presence causes formation of salted out and faded spots on the surface of the articles during firing. Different methods are used to prevent these negative phenomena: conversion of soluble into insoluble salts, protection of the two faces of the just molded brick by application of a face layer.

However, these methods have many drawbacks: the salts contained in the clays are not completely converted into the insoluble state in the bulk brick paste; coating the face of articles with light- or red-firing clays is accompanied by peeling; in case of mechanical damage, the surface of the basic brick not protected by a coating is uncovered. However, we should note that face brick is one of the most durable and optimum types of articles used for finishing buildings in comparison to wet stucco and has good architectural and decorative properties.

It was found in [1] that use of face brick in construction allows reducing the cost of 1 m^2 of wall by 15%, labor by 25%, and also reduces expenditures for maintenance of facades to the minimum.

Methods of bulk dyeing and bleaching of the clay paste followed by incorporation of a ceramic pigment and secondary production products and using combinations of clays of different chemical and mineral composition, Tripoli, etc., are used for manufacturing facing brick [2].

Research has also been conducted at the Scientific-Research Institute of Construction Ceramics on bulk dyeing of ceramic paste with manganese ore, which would result in brown to black facing brick. The optimum amount of manganese ore was 3 – 7%.[2] It was found that the firing temperature significantly affected the color of the face brick.

Chromium and iron minerals, different limestones, electroplating plant wastes, and relatively cheap readily available dyes can be used as chromophoric additives to pastes.

It is recommended that additives be incorporated in the form of slip or finely ground powder, with careful stirring of the suspension, to ensure uniform coloration of the ceramic paste.

Articles fired a uniform dark red were obtained by incorporating 10% hematite iron ore in paste based on low-melting clay. The compressive strength of the articles fired at a temperature of 950°C attained 26.8 MPa, water absorption was 9%, bulk weight of 1480 g/m^3, and cold resistance was 35 cycles. Articles satisfying such indexes have a grade of 200 [2].

Wastes can be added instead of iron ores: electroplating sludges, ferrosols, and slags. The most effective dyeing is attained with electroplating sludges containing 70 – 80% iron oxides. Electroplating sludges, which are a pasty mass, can be added after drying and grinding in fabrication of articles by semidry molding or in the form of a suspension in plastic

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[2] Hear and below — the weight content.

molding. However, the color of the surface of the brick changes from red to dark brown during firing at 950 – 1150°C.

A similar color effect was attained in manufacturing brick with combined use of clays that differ in chemical and mineral composition and corresponding manufacturing properties. As a result of the studies conducted at Belarus Research Institute of Construction Materials RUP [1], brick of a saturated monochromatic dark red color with water absorption of 6 – 8% and cold resistance of approximately 100 cycles was obtained by combining high-melting and low-melting clays and argillaceous sands. In particular, the high-melting clay used is a medium-plastic, medium-disperse clay highly sensitive to drying. Its chemical composition is (%): 7.2 – 7.7 Fe_2O_3, 65.0 – 67.0 SiO_2, 16.0 – 17.0 Al_2O_3, and with respect to the mineral composition, it is a polymineral clay with a predominant content of montmorillonite. The second, low-melting clay contains minerals of the hydromica, kaolinite, and carbonate group. The chemical composition is characterized by a high content of dyeing oxides: 7.2 – 8.5% ($Fe_2O_3 + TiO_2$). The amount of silicon and aluminum oxides is 53 – 56 and 13 – 14%, respectively.

Argillaceous sand is represented by coarsely disperse polymineral clay raw material with a predominant content of montmorillonite. Light red brick was obtained with low-melting clay and argillaceous sand. Stable properties of the fired material were ensured by correcting the conditions of preparing the ceramic paste, drying, and firing. To manufacture light colors of brick, addition of up to 5% carbonates was recommended in [3]. Technology for production of high-quality brick made from argillaceous sands with a high calcium oxide content was also proposed in [4]. The average chemical composition of the argillaceous sand is as follows (%): 67.38 SiO_2, 13.37 ($Al_2O_3 + TiO_2$), 3.75 Fe_2O_3, 5.60 CaO, 1.57 MgO, 0.30 SO_3, 8.20 calcination loss. The mineral composition of this component is represented by kaolinite, quartz, calcite, and anorthite.

Quartz sands are recommended in [5] for production of face ceramic brick, and the total content of 0.630 – 0.315 and 0.315 – 0.140 mm fractions is a minimum of 80 – 85%.

Light shades of brick can also be obtained by bleaching red-firing clays with a mineralizer additive represented by lithium chloride combined with waste characterized by a high calcium oxide content (5 – 20%) [6]. The samples were fired at 600 – 900°C and held at the maximum temperature for 1 h. As a function of the amount of calcium carbonate and lithium chloride added with an optimum content of up to 20.0% $CaCO_3$ and 0.2% LiCl, the color of the samples obtained changed from red-brown to white-yellow. It was noted that lithium chloride intensifies the sintering process and passage of α-Fe_2O_3 (hematite), which gives the paste red-brown dyeing, into the glassy phase, and free lime enhanced the bleaching effect. However, the water absorption of the samples increased to 20% and the porosity increased to 39%.

To obtain brick uniformly colored over the entire volume and increase the physical and technical indexes, we added Latnenskoe fireclay, Prosyanovskoe kaolin, quartz, sand, and chalk to low-melting clay. Readily available green, yellow, and light blue pigments were used as dyes and were added in the amount of 0.5 – 5.0% above 100%. The chemical composition of the materials used is reported in Table 1.

Light-brown low-melting clay contains the following basic minerals: α-quartz, illite, kaolinite, calcite, and montmorillonite, which was confirmed by x-ray phase analysis (Fig. 1).

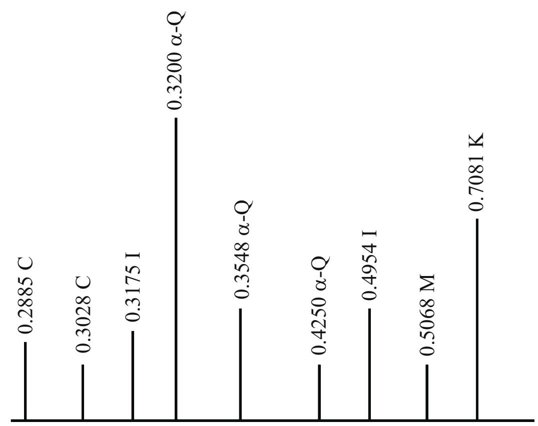

Fig. 1. X-ray diffraction diagram of low-melting clay: C) calcite; M) montmorillonite; I) illite; α-Q) α-quartz; K) kaolinite.

TABLE 1

Raw material	Mass content, %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	calcination loss
Clay:									
low-melting	57.65	14.91	5.51	0.72	6.61	1.83	3.80	0.70	8.21
Latnenskoe	49.00	34.74	0.76	1.74	0.86	0.13	0.59	0.51	11.67
Prosyanovskoe kaolin	47.00	38.00	1.00	–	–	0.40	1.50	1.00	10.20
Chalk	2.21	0.30	0.15	0.99	53.46	1.19	–	–	42.41
Quartz sand	96.38	1.47	0.05	–	0.50	–	0.15	0.13	1.32

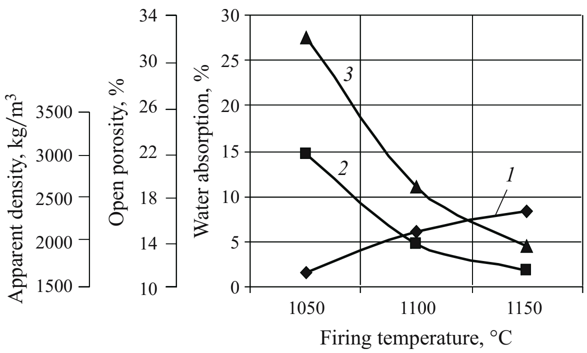

Fig. 2. Physicochemical properties of the ceramic material: *1*) apparent density; *2*) open porosity; *3*) water absorption.

According to the results of differential thermal analysis, the derivatogram of low-melting clays has endothermic effects at 130, 530, and 808°C, which corresponds to elimination of hygroscopic moisture during decomposition of clay minerals and calcite. The exothermic effect at 310°C indicates burnoff of organic contaminants.

With respect to the granulometric composition, the clay belongs to the disperse category (40 – 88% content of fractions smaller than 0.01 mm, 20 – 60% content of fractions smaller than 0.01 mm), it is low-sensitivity with respect to the sensitivity to drying ($K_s < 1$), and is medium-plastic with respect to the plasticity (21 – 22%).

The characteristics of Latnenskoe clay and Prosyanovskoe kaolin have been investigated in some detail.

The mineral composition of the chalk is represented by calcite, and there is an endothermic effect (930°C) corresponding to its decomposition on the derivatogram.

Quartz sand is represented by particles with a grain size of 0.01 – 2.00 mm and the mineral composition is basically α-quartz and feldspar, mica, and other mineral impurities. To enhance sintering and reduce the porosity, 3 – 7% cullet was added to the pastes. The best bleaching effect was obtained with Prosyanovskoe kaolin and chalk in a ratio of 1 : 4.

The curves of the basic physical and technical properties of the materials on the firing temperature are shown in Fig. 2. When the firing temperature increased to 1150°C, water absorption decreased to 2.3%, open porosity decreased to 10.7%, and the density increased to 2400 kg/m^3, which corresponds to the properties of clinker brick. The brick obtained is characterized by good properties that ensure cold resistance of more than 50 cycles of alternate freezing and thawing, which corresponds to the indexes of grade M250 brick. This brick can be used for external masonry of walls, since it has elevated architectural and decorative characteristics and durability.

TABLE 2

Transition metal salts	Color coordinates		Dominant wavelength, nm	Purity of color, %
	x	*y*		
Co^{2+}	0.129	0.197	480	70
Cr^{3+}	0.243	0.573	530	75
Fe^{3+}	0.523	0.349	610	69
Ni^{2+}	0.311	0.479	550	60

To obtain colored brick, ceramic pigments (sludges) are added to the paste in the amount indicated above while stirring and fired at 1100°C with holding at the final temperature for 1 h.

It was found that when Latnenskoe fireclay was used, the water absorption and porosity increased and the apparent density decreased.

An analysis of the results obtained showed that one component of the paste can be impregnated with solutions of transition metal salts first to ensure high-quality coloration of the brick and to combine synthesis of the ceramic pigment. In comparison to kaolin, Latnenskoe fireclay containing up to 2.5% dyeing oxides is a more readily available and cheaper raw material component.

Clay previously impregnated with solutions of transition metal salts, which has good wettability, was dried (100 – 120°C), ground, sieved, and added to the batch together with chalk in the ratio of 1 : 4. A 35% solution of the salts $K_2Cr_2O_7$, $Fe(NO_3)_3 \cdot 9H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 7H_2O$ in the amount of 5 – 15% in terms of oxides was used for impregnating the pastes. The composition of the ceramic paste batch was as follows (%): 63 – 72 low-melting clay, 20 – 30 quartz sand, 3 – 7 cullet, 7 – 10 colored Latnaya clay. The prepared paste was mixed, followed by molding of articles by the plastic method (18 – 20% moisture content), drying, and firing at 1050 – 1150°C.

Introducing significant changes in the colored brick technology regulations is based on an analysis of the results of preliminary synthesis of ceramic material based on Latnaya clay impregnated with salts, fired at 1050°C, and held at the maximum temperature for 1 h.

The color characteristics of the pigments used are reported in Table 2.

In addition, we proposed readily available ceramic pigment compositions based on silicate materials [7].

In addition to manganese and iron ores, sludges and slags from metallurgical enterprises can thus be used for bulk dyeing of ceramic brick.

Since brick clays contain a large amount of Fe_2O_3 in the form of hematite, ceramic materials turn red during firing, which does not allow obtaining another color scale on addition of pigments. For this reason, preliminary bleaching of low-melting clays with chalk, kaolin, mineralizing additives, or addition of dyes is recommended.

Not only chalk, but also fireclay or kaolin with a pigment added should be used for bleaching clays as this intensifies the sintering process, reduces the porosity of the brick, increases its cold resistance, and ensures uniform dyeing.

It is also useful to impregnate the fireclay or kaolin with solutions of transition metal salts, which makes it possible to combine synthesis of pigments and firing.

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